



... for a brighter future

Experience Using AAO for MCP's

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Pico-Second Workshop VII

The Development of Large-Area psec Photo-Devices

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U.S. Department
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Science**

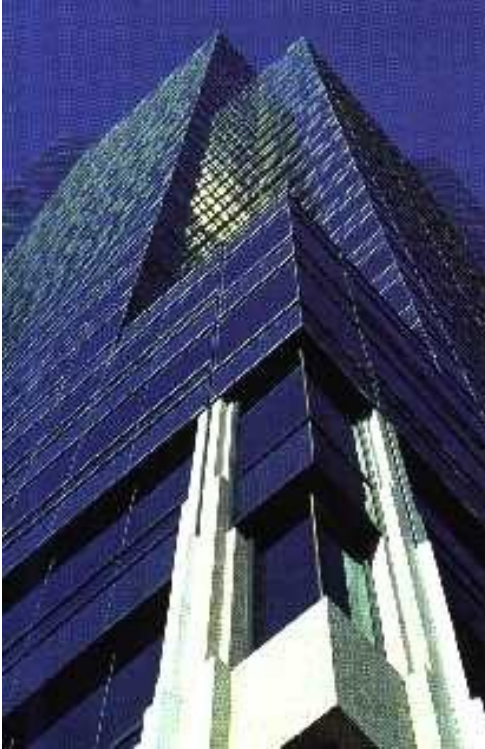
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Outline – AAO synthesis for MCP application

- Brief introduction on Anodized Aluminum Oxide (AAO)
- Control of pore distance through anodization potential – bottom up
- Mild and hard anodization
- Control of pore distance through surface patterning – top down
- Summary

Commercial Applications of Anodized Aluminum Oxide (AAO)



Architectural products:
windows and doors
Surface protection and
coloring



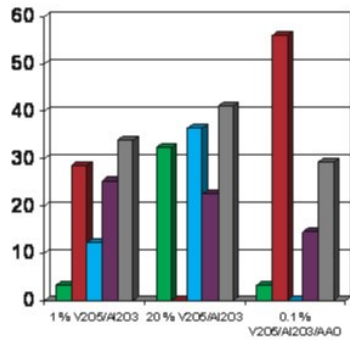
NASA Space Station:
trusses and handrails



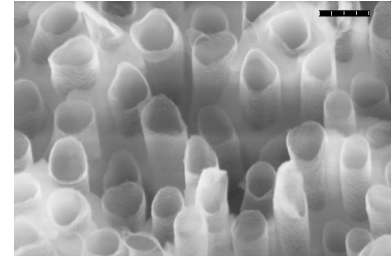
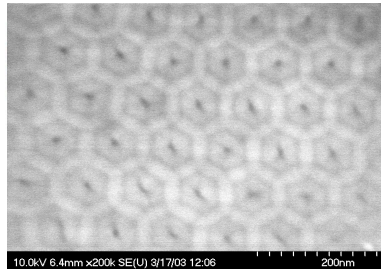
Appliances, aircraft,
automotive, lighting,...

Aluminum Anodizers Council

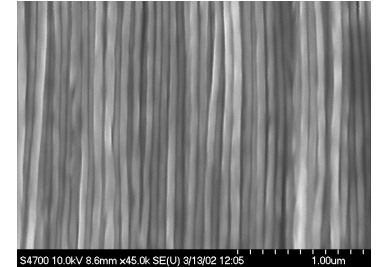
Research Activity Based on Nanoporous Templates



ALD coated AAO
- Catalysis

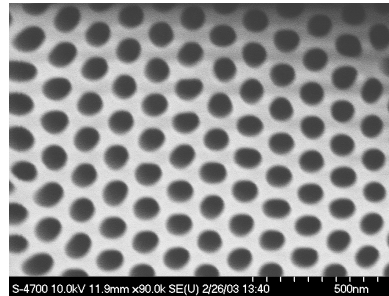


Bi 200 nm

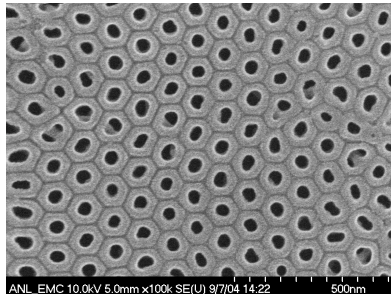


Ni 60 nm

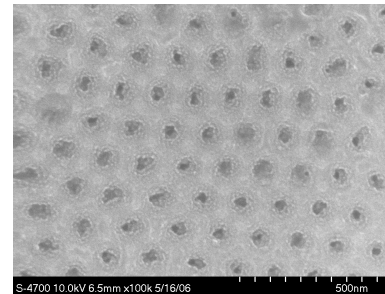
Nanotubes and nanowires



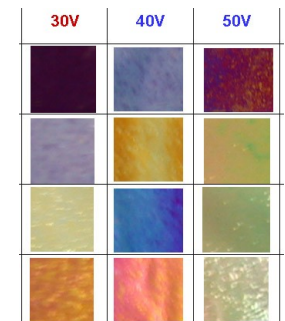
AAO Template



Pd nanowells



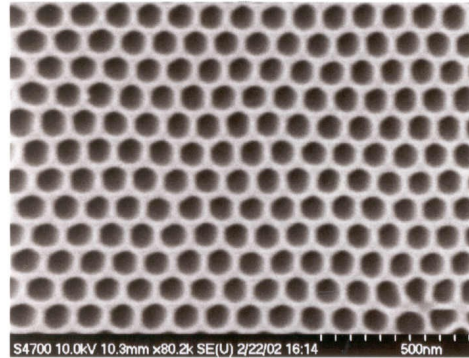
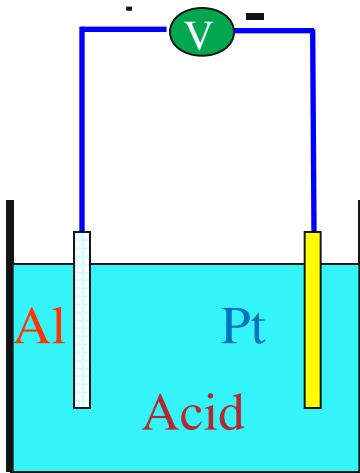
AAO nanowells



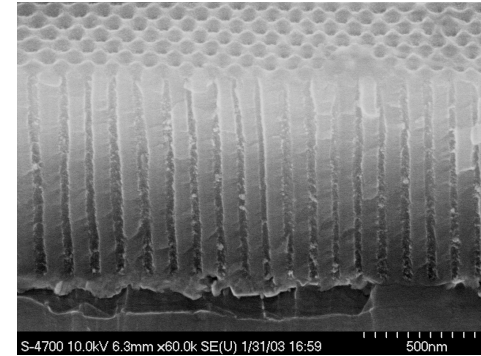
-Interference colors
-Chemical sensors

Introduction - Preparation and Cell Structure of AAO

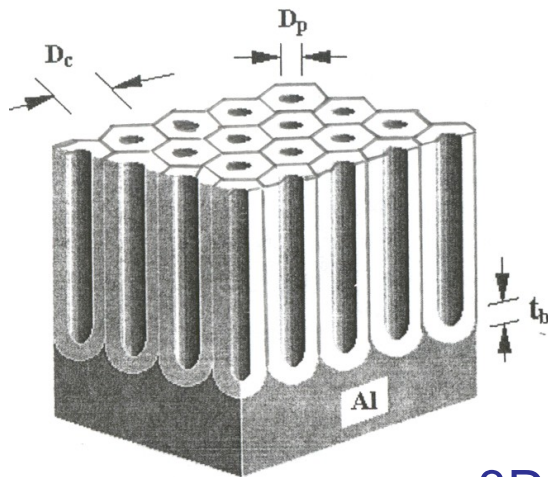
Anodization of Aluminum



SEM of AAO thin film



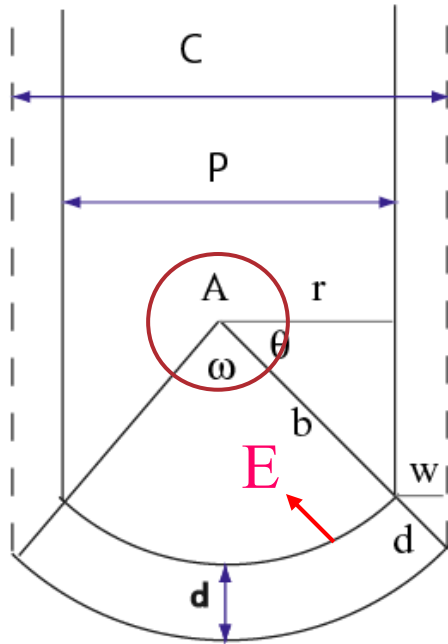
AAO cross section



3D model

- ❖ Highly ordered nanopores
20–200 nm (mild anodization)
220–300 nm (hard anodization)
- ❖ Very high aspect ratio
> 1,000
- ❖ Lack of long range order
- ❖ Ideal for nanowire, nanotube template synthesis

Model by O'Sullivan and Wood (1970)



C cell diameter

P pore diameter

A center of curvature

b radius of curvature

d barrier layer thickness

w cell wall thickness

$w = d \cos \theta$,

experimentally $w = 0.71 d$

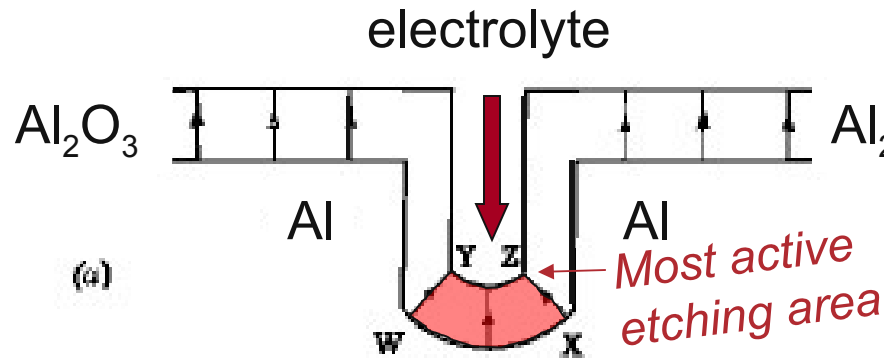
$\theta = 44.8^\circ$

$$J = \frac{I}{(\omega / 4\pi) 4\pi b^2}$$

$$= \frac{I}{\omega b^2}$$

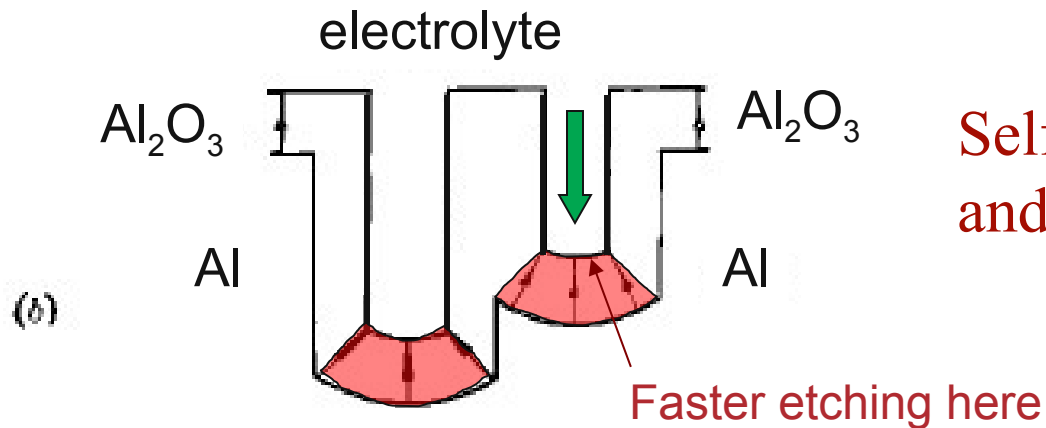
$$E = \frac{J}{\sigma} = \frac{I}{\sigma \omega b^2}$$

Cell and Pore Growth Mechanism



Lines of force of the Electric field

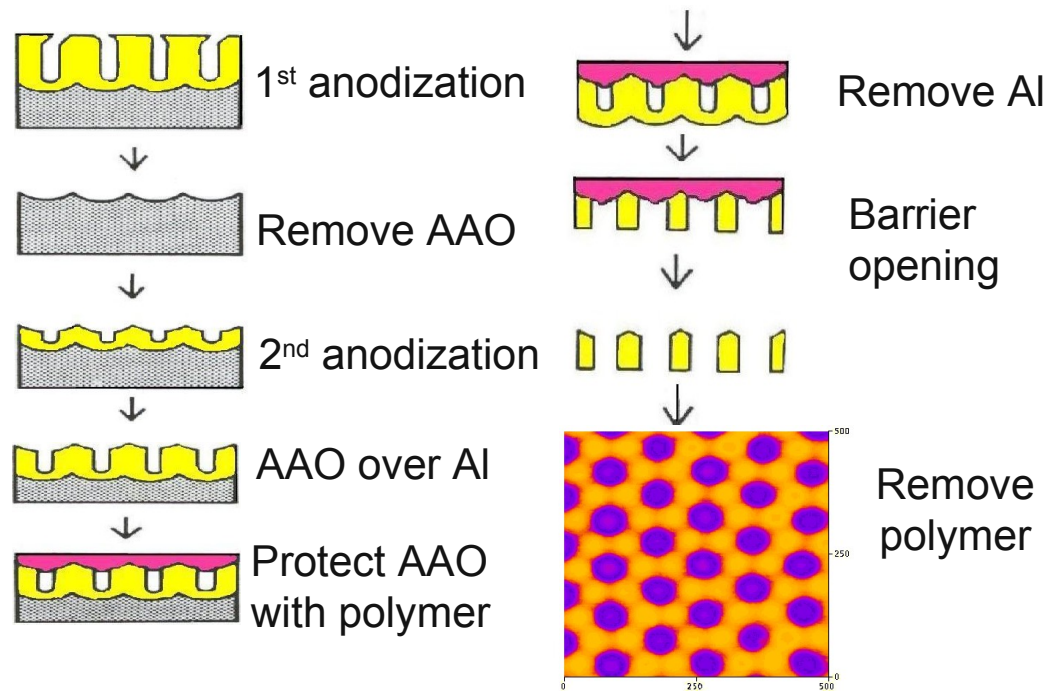
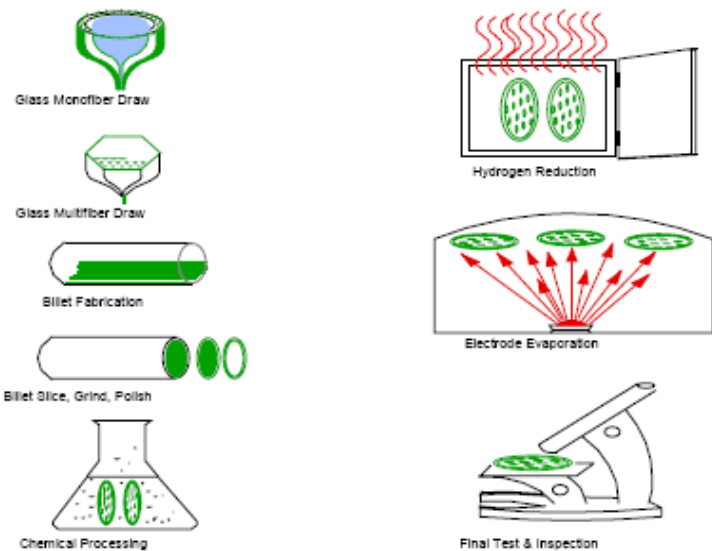
Self sustaining pore growth



Self adjusting pore size and cell distribution

Preparation of glass MCP vs AAO

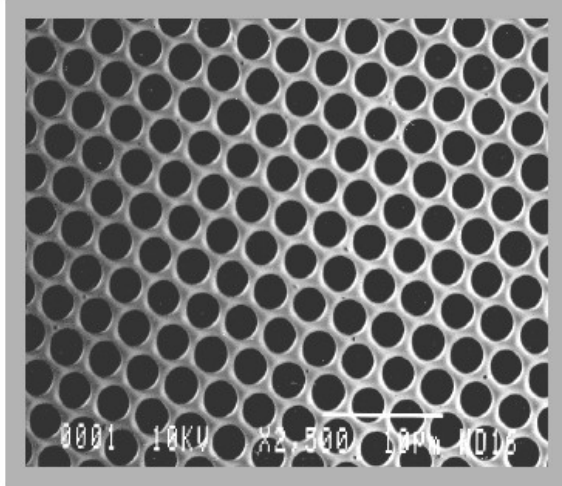
BURLE Electro-Optics



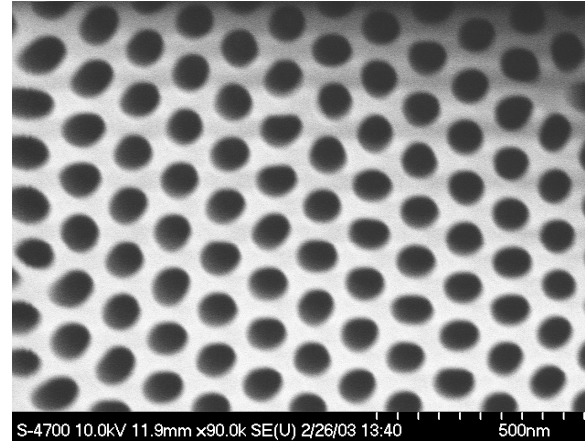
- development of specialty glasses
- fiber glass drawing
- assembly into hexagonal array
- fusion into a boule
- wafer slicing and processing
- Pore diameter 25-2 μ m
- Aspect ratio 100-40

- ❖ Multi-step wet chemical etching
- ❖ Self assembly and no special equipment
- ❖ Pore diameter 300-10 nm
- ❖ Aspect ratio 1,000-10

Advantage for smaller pores



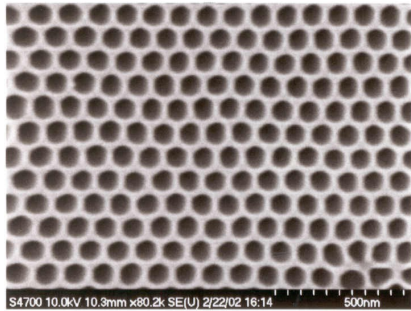
2.3 micron MCP from Burle
Electro-Optics



AAO template with 80 nm pore
diameter and 143 nm pore-to-pore
distance

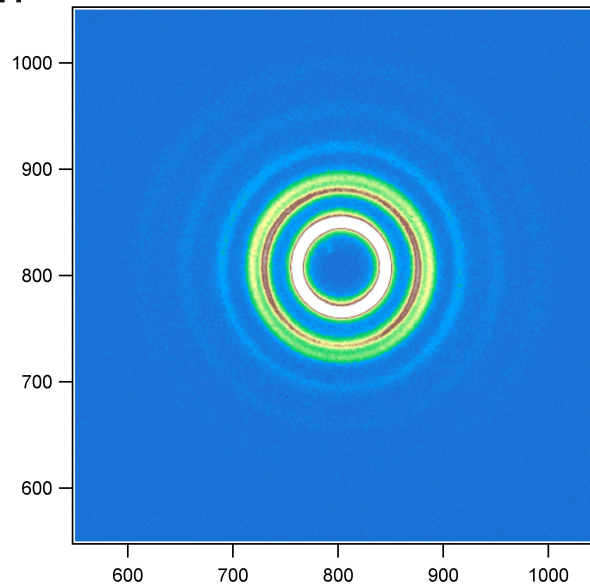
- The temporal response of the device is determined by the pore size and smaller pore size makes faster time response
- Smaller pore improves spatial resolution
- Smaller pore recharges faster than that of the larger pores and the device dead time is reduced.

AAO Characterization –

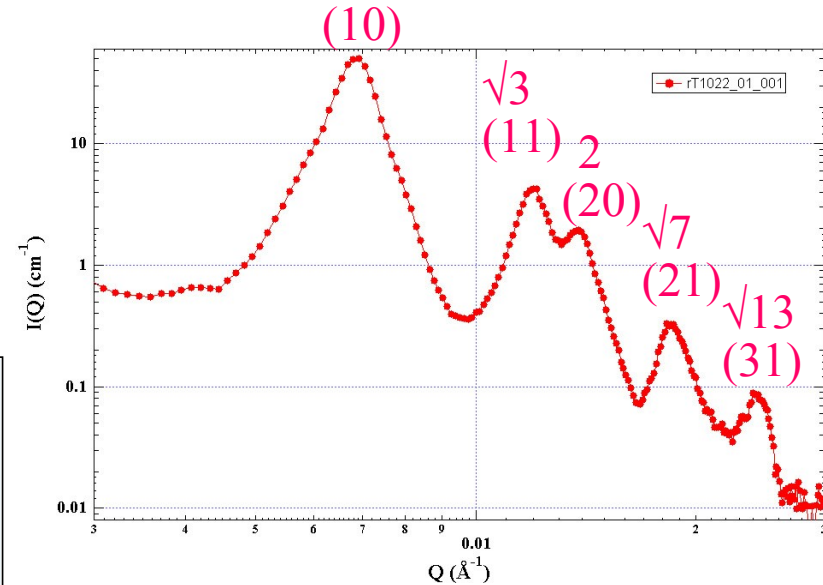


FESEM image
of AAO $1 \times 1.5 \mu\text{m}^2$

2D image of
an AAO SAXS
pattern



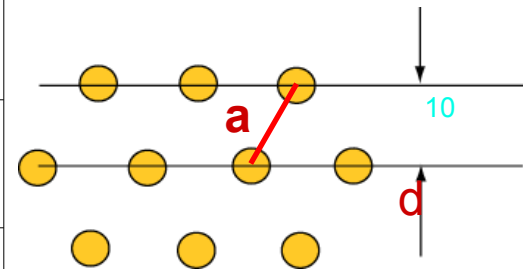
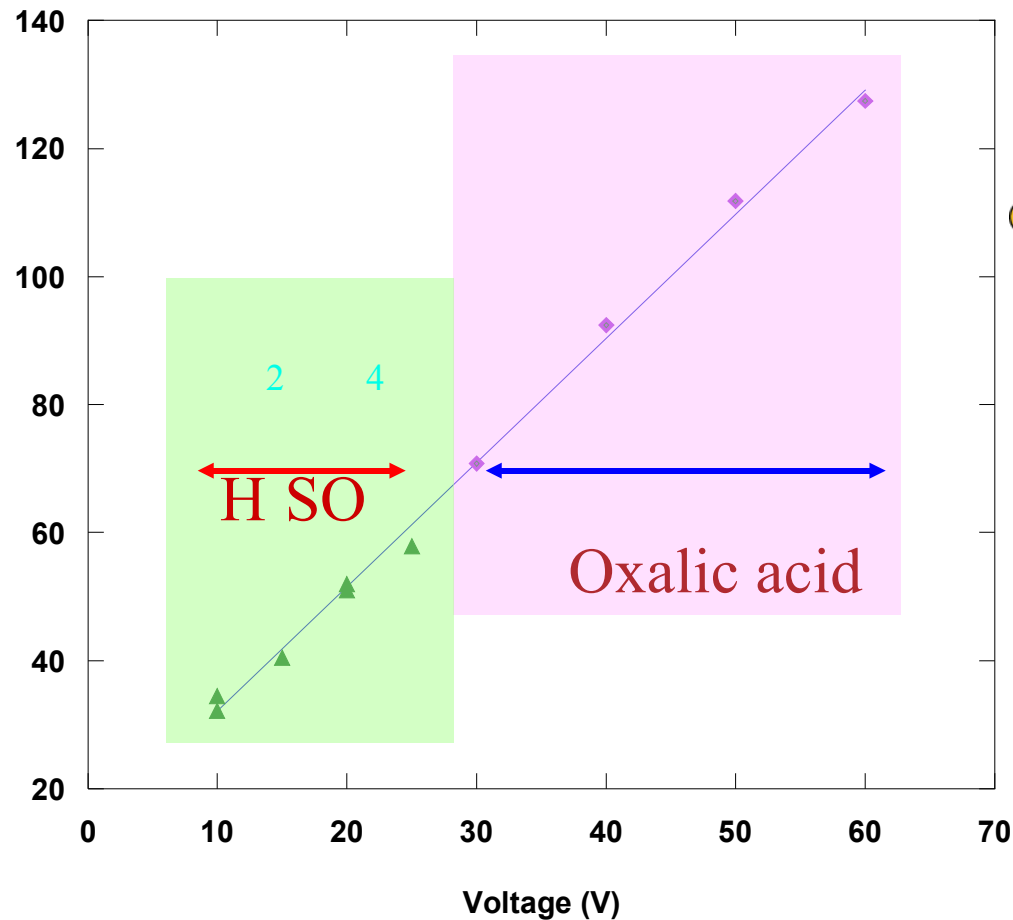
AAO prepared in oxalic acid



SAXS intensity vs. q

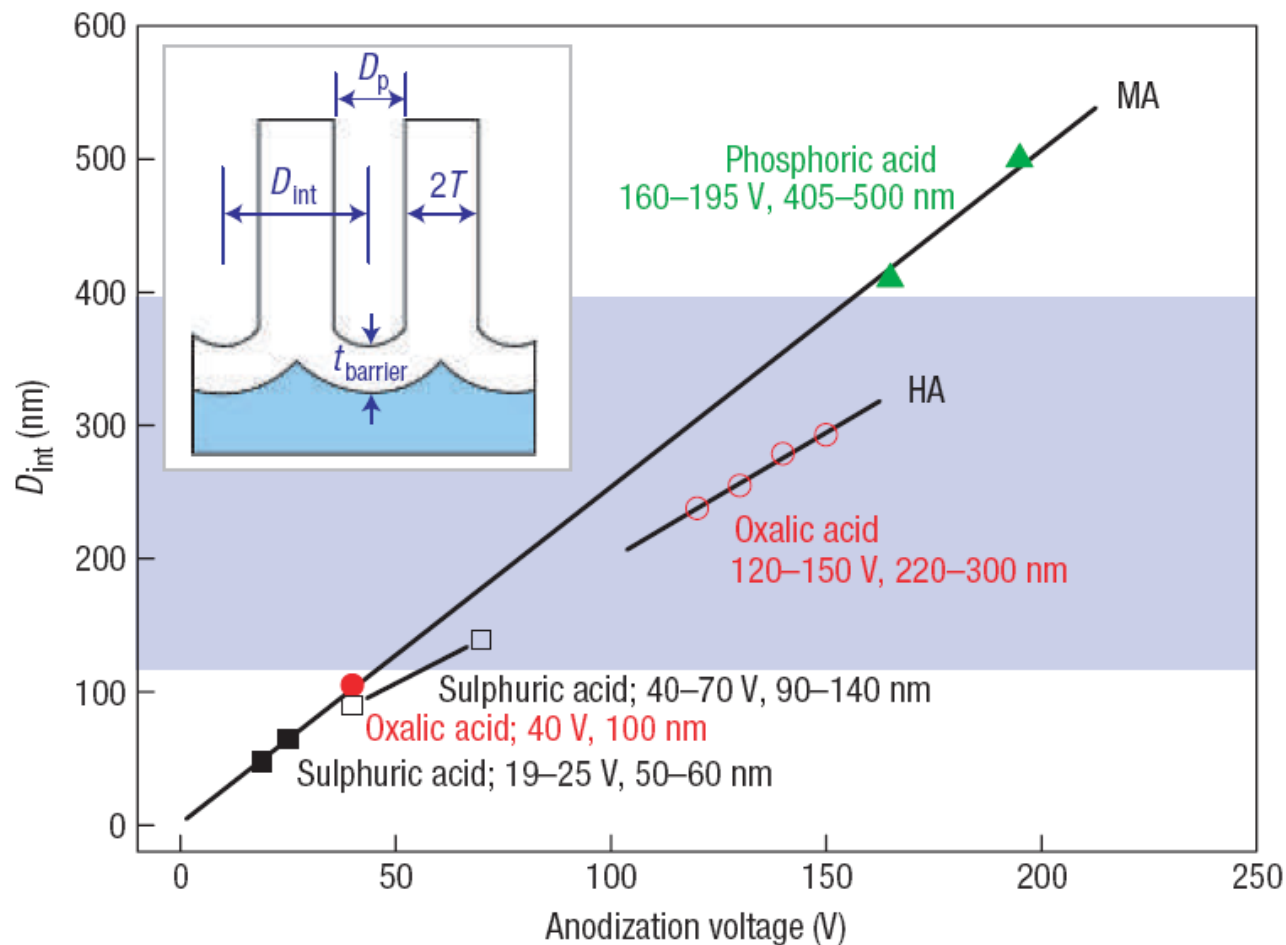
Control of pore distance through anodization potential

Mild Anodization



Anodization media and applied potentials provide precise control of the AAO pore distance.

Control of pore distance through hard anodization

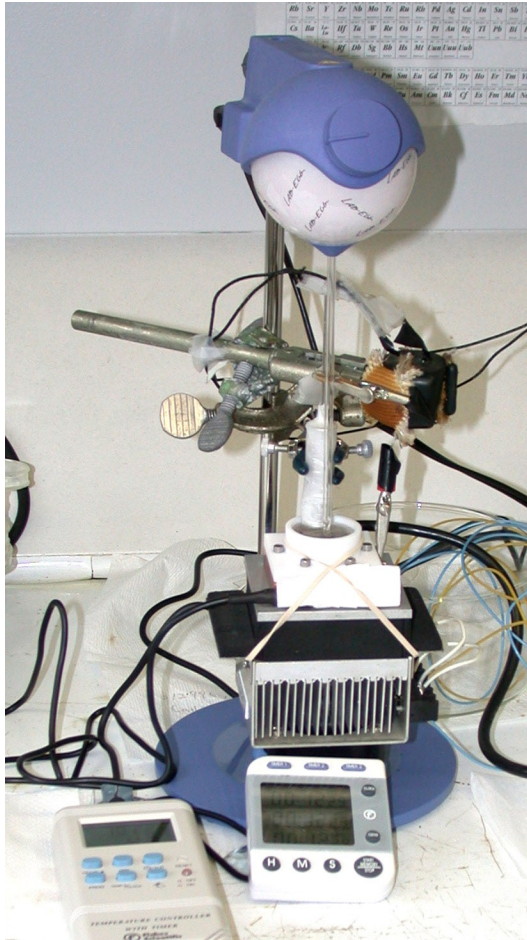


- HA is difficult to control
- HA is much faster and provides large pore-to-pore distance

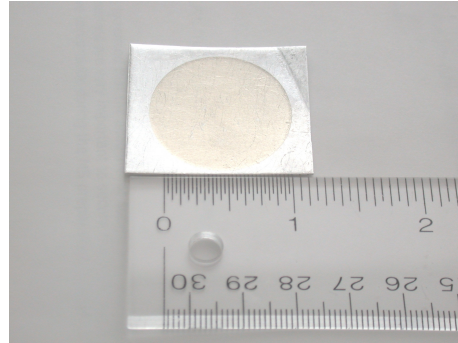
W. Lee et al. Nat. Mater.2006

Hard Anodization – oxalic acid, 140 V

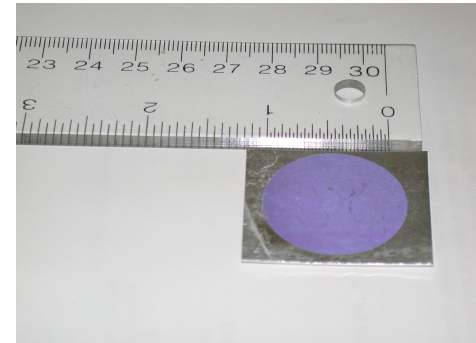
Al surface after the 1st anodization
with alumina removed



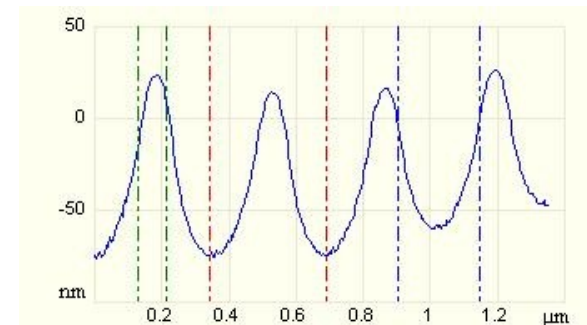
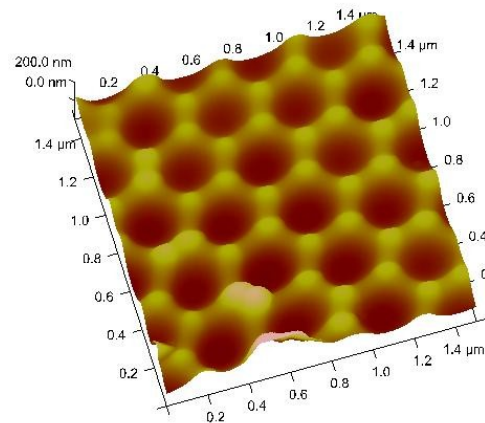
HA setup



Viewing against the light

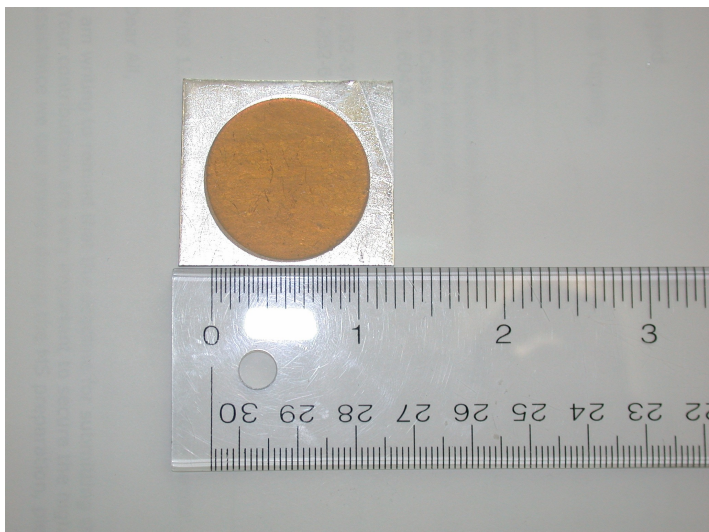


With flash light

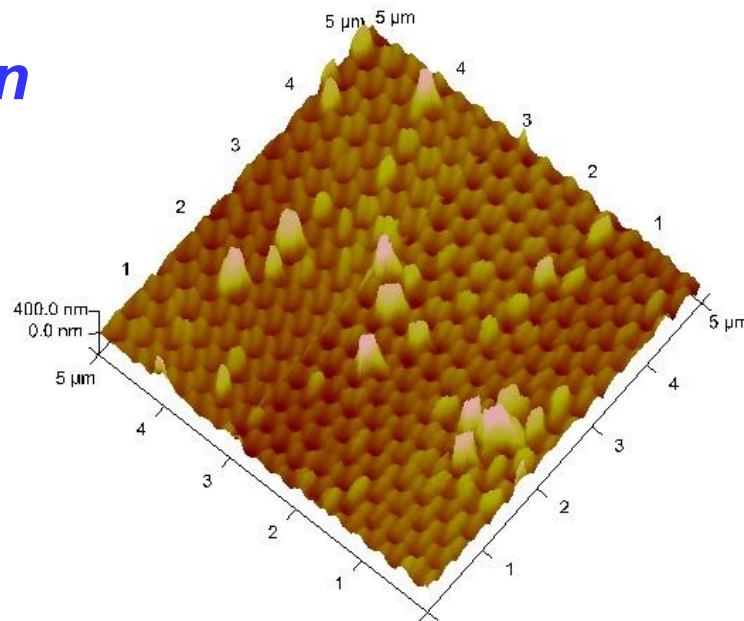


- AFM of the Al surface
- Pore-to-pore distance 348 nm
- Pore diameter 244 nm

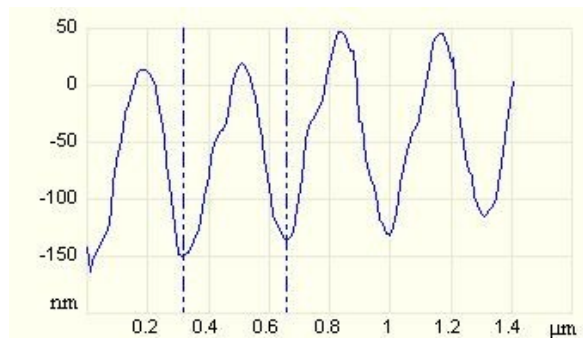
HA after the second anodization



AAO membrane ($40\text{ }\mu\text{m}$ thick)
over Al substrate

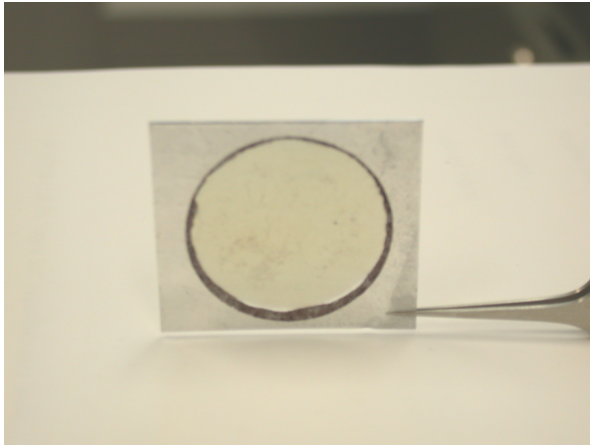


AFM topography showing the top surface
of AAO membrane



Pore-to-pore distance 330 nm
Prepared at 140 V DC, 3 hrs

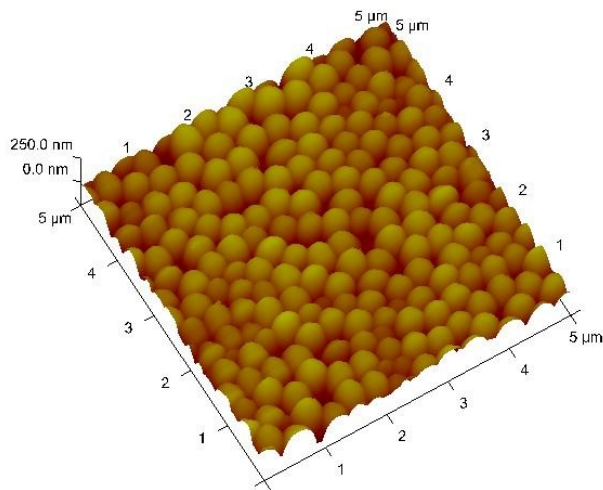
After Al removal – the barrier side



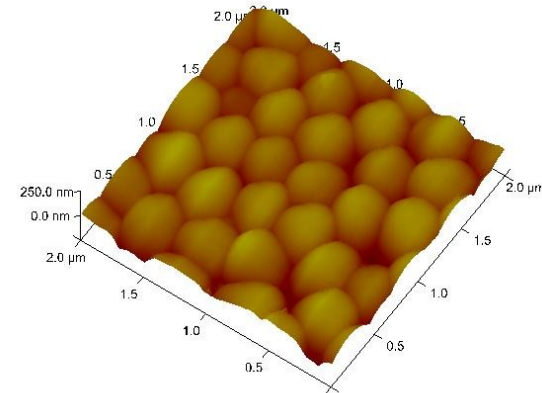
AAO membrane in Al frame



Semitransparent AAO membrane

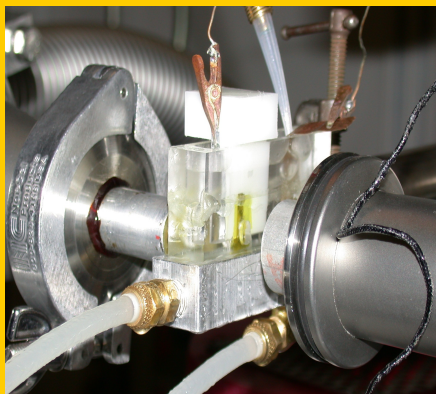


AFM of AAO barrier (bottom) layer

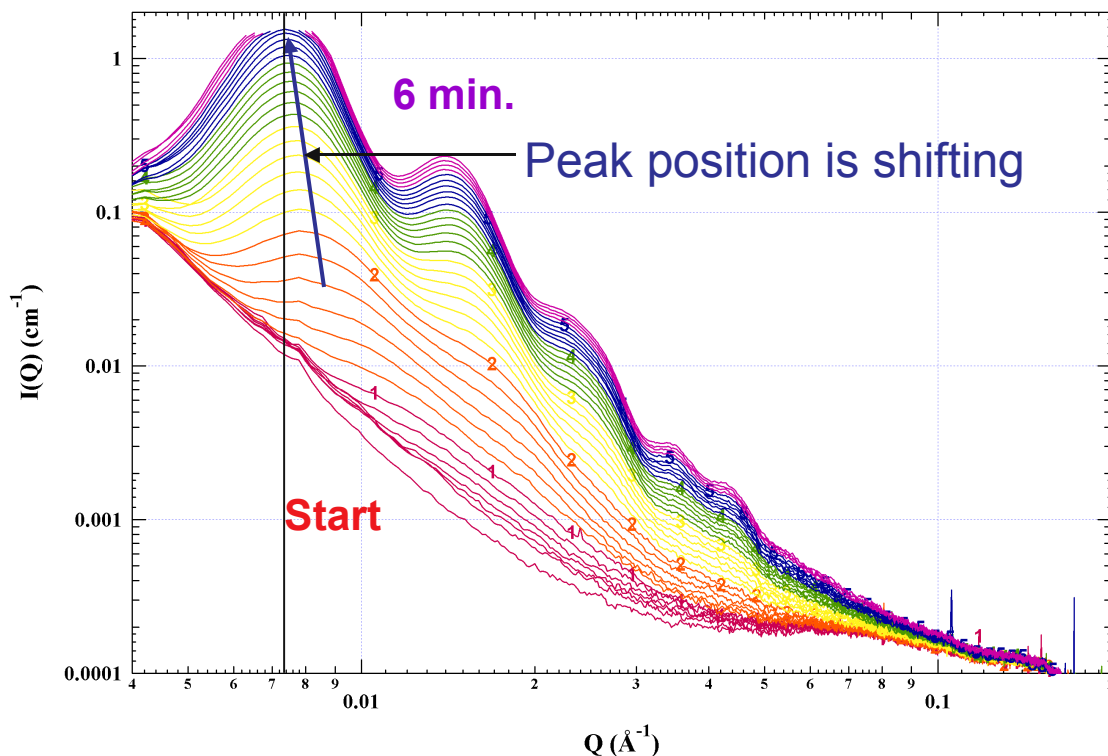


2x2 micron scan showing barrier layer with 350 nm pore-to-pore distance, 50-80 nm barrier height

Effect of patterning – In-situ Transmission SAXS



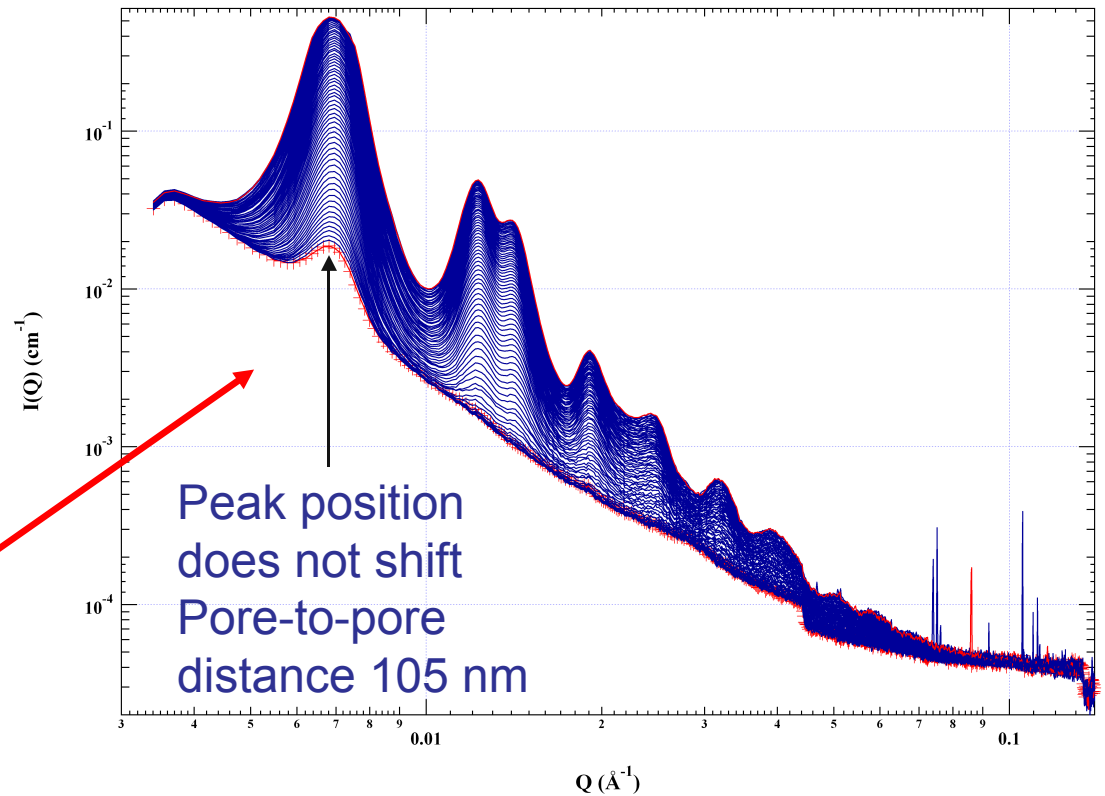
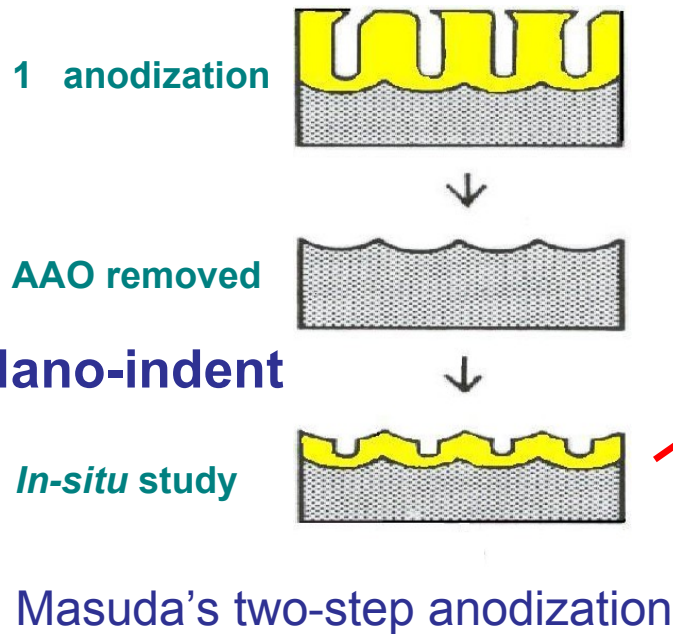
Electrochemistry sample cell



The first 6 minutes of AAO growth in oxalic acid at 40 V, showing pattern developed but not ordered.

Scattering peak position is shifting in the first 6 minutes from smaller pore-to-pore distance (84 nm) to larger pore-to-pore distance (99 nm).

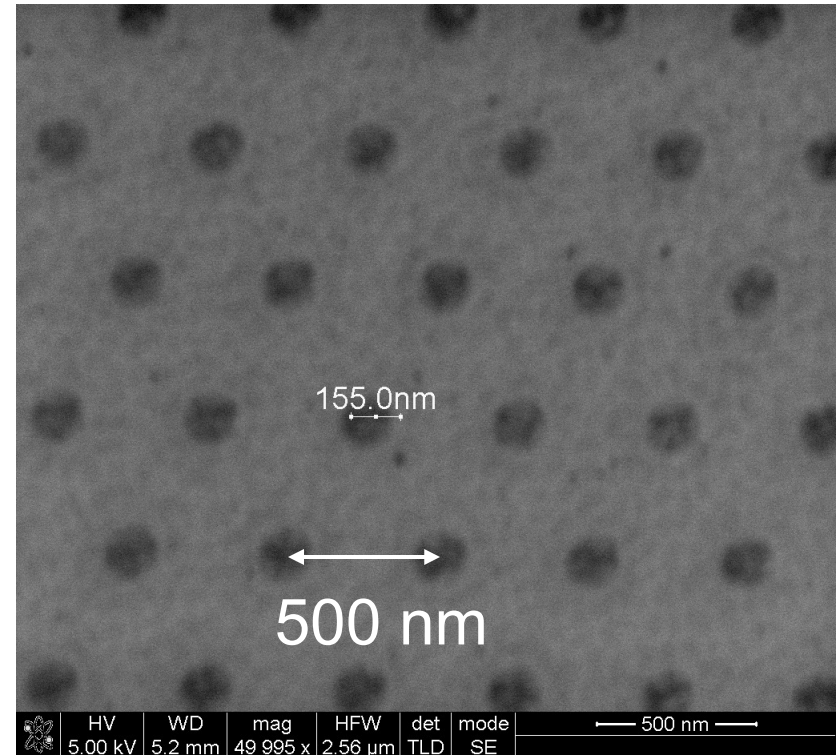
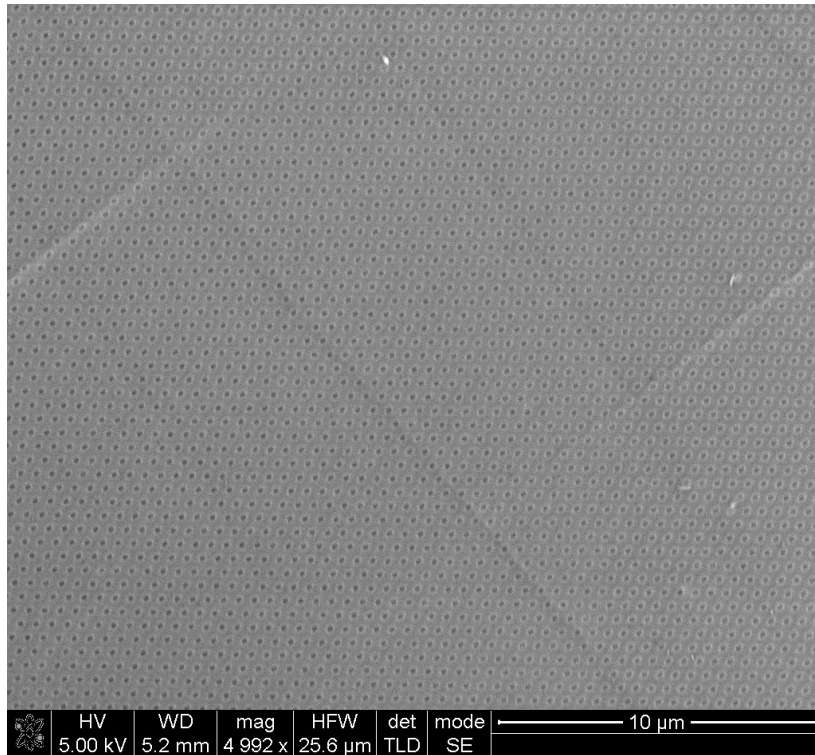
In-situ SAXS of pre-patterned Al



The first 6 minutes of pre-patterned AAO growth in oxalic acid at 40 V showing highly ordered hcp pattern.

For the pre-patterned substrate, the peak position does not shift with time!
Highly ordered pores form within 1 minute.

Top-down Focused Ion Beam (FIB) approach to prepare 0.5 micron pore distance



- Perfect pore array can be prepared
- Very time consuming & expensive
- Useful for new pattern design and testing

Other top-down options

- FIB is a serial technique – slow for large area
- Laser writer is also a serial technique but much faster
- Photolithography is fast, a mask must be prepared
- Nanoimprint is fast, also needs a master stamp
- All these techniques are available to us at the ANL Center for Nanoscale Materials (CNM)

Summary

- AAO is a good candidate for new MCP materials
- Large area with improved temporal, spatial resolution possible
- Small pores will reduce detector dead time
- Both bottom-up and top-down approaches can be applied to develop new large area photodetector

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